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A COMPARISON OF DATA REDUCTION TECHNIQUES FOR LINE EXCITED OPTO--ETC(U)

JAN 82 S B TILDEN, M B DENTON

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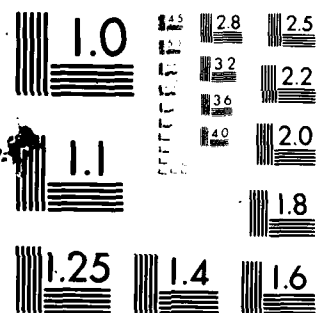
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by

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for Line Excited Optoacoustic Analysis of Mixtures**

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ABSTRACT

The use of discrete line laser excitation for the optoacoustic analysis of gas mixtures holds promise as a formidable analytical tool. However this technique presents challenging demands on the data reduction process to increase the reliability of the analytical results. The problems unique to this method which made data reduction difficult are discussed. Use of simultaneous equations, multivariate least squares and a new iterative coefficient weighted least squares approach are compared. Data indicating the relative performance of these methods are presented.

Index headings: Optoacoustic Spectroscopic Mixture Analysis.

Introduction

Optoacoustic Spectroscopy is theoretically a sensitive technique (1) capable of quantitatively determining a wide variety of gases. However there has been little work directed towards utilizing optoacoustic spectroscopy for the analysis of gas mixtures. This is especially true in cases where a large amount of spectral overlap exists between many of the components. Since the ability to analyze gas mixtures is a highly desirable feature when employing the optoacoustic technique, a comparison of various data handling strategies is needed to determine the limitations of these strategies under actual analysis conditions.

Theory

The analysis of mixtures using any spectroscopic technique becomes trivial when absorption regions of one analyte species are not overlapped by other analyte species in the mixture. The wide acceptance of the atomic absorption technique is in part due to the fact that complicated mixtures of metals and some anions can be determined without any prior separation step. The limited number of situations where spectral overlap of atomic transition occurs can usually be avoided by simply finding other atomic lines where spectral overlap is minimized.

Most present-day optoacoustic systems employ a low pressure IR molecular gas laser as the light source. Due to the nature of these laser sources, only a discrete number of laser lines may be selected. This

can limit the ability of the analyst to find a laser line where only one component of the gas mixture will absorb, although it is possible to find selected mixtures where spectral overlap is minimal (3). The spectral overlap problem is further compounded in optoacoustic spectroscopy by the relatively broad vibrational-rotational absorption bands when analyzing gas mixtures near atmospheric pressure.

The classical approach for determining the component concentrations of mixtures where spectral overlap is significant is to solve sets of simultaneous equations:

$$\begin{array}{l} C_{11}X_1 + C_{12}X_2 + \dots + C_{1n}X_n = A_1 \\ \vdots \\ C_{n1}X_1 + C_{n2}X_2 + \dots + C_{nn}X_n = A_n \end{array} \quad (\text{Eq. 1})$$

where the general term C_{ji} is the absorption coefficient of component i at wavelength j ; X_i is the concentration of each component i ; and A_j is the measured absorption value at each wavelength j . Typically the number of equations equals the number of unknowns. Perlmutter, Shtrikman and Slatkine (4) used the simultaneous equations approach to determine the presence of ethylene in fruit storage warehouses. Other interfering gases included CO_2 , H_2O and a wide range of trace pollutant gases which were treated collectively as one gas in the analysis. This study showed that ethylene could be determined in the presence of these other gases under certain conditions. The authors concluded that the accuracy of the analysis of ethylene was limited by the accuracy in determining the spectral signatures of interfering gases (i.e. the absorption coefficients at each wavelength used in the analysis). The authors also indicated that negative concentrations of CO_2 were sometimes

determined after solving the four simultaneous equations. A kinetic cooling argument was used to explain this behavior (5). It can also be shown that negative results can be explained by a failure of the simultaneous equations approach to properly determine the mixture.

A possibly better mathematical approach for determining the constituents of mixtures involves the use of least squares multivariate analysis (6). This technique was first used for mixture analysis using spectroscopic data by Sternberg, et al. (7) and more recently by Warner et al. (8). Although this technique is well established it has not been used for optoacoustic mixture analysis.

The least squares multivariate approach provides for the incorporation of more equations than unknowns in the analysis. Since as much data as is available can conceivably be used, one would intuitively conclude that this mathematical technique should be superior over the simultaneous equations approach. The results of actual mixture analyses will confirm this.

The derivation of the multivariate least squares system has been presented elsewhere (7). The result of the least squares operation is the transformation of a non-square set of equations (more equations than unknowns) into a new set of equations, where the number of equations equals the number of unknowns. The form of this new equations set is as follows:

$$C' \cdot C \cdot X = C' \cdot A \quad (\text{Eq. 2})$$

where matrix C is the original coefficient matrix, C' is the transpose of C, X is the unknown component vector and A is the measured or observed vector. To determine X (the unknown concentrations of each component in the mixture) involves a matrix inversion step:

$$X = [C' \cdot C]^{-1} \cdot C' \cdot A \quad (\text{Eq. 3})$$

Although the matrix inversion step can be tedious, a new matrix, U, can be defined:

$$U = [C' \cdot C]^{-1} \cdot C' \quad (\text{Eq. 4})$$

The matrix U needs to be determined once for each mixture system.

It will be shown that the least squares multivariate analysis can give more accurate results when determining the component concentrations of a mixture. However its most useful feature is the concurrent generation of statistics which gives the analyst some indication of the reliability of the results. The utility of the statistics generation step will be apparent when results of mixture analyses using the multivariate least squares approach are presented.

Additionally it is possible to weight the least squares analysis to achieve an even more optimum result. Weighting schemes usually involve a weight factor assigned to each observable. Weighting factors can be collected into a weighting matrix W. When applied to the least squares analysis, these weighting factors will weight most heavily those equations in which the variance of the observable is a minimum.

$$X = [C' \cdot W \cdot C]^{-1} \cdot C' \cdot A \quad (\text{Eq. 5})$$

The optimum form of the weighting matrix W has been studied (9). This study showed that different values of the weighting matrix W can also heavily influence the results of the analysis. It was suggested that the optimum weighting matrix W should include the reciprocal variances of each observable.

Perlumetter et al. (4) showed that the limiting factor in achieving a reliable mixture analysis with optoacoustic spectroscopy is the difficulty in accurately determining spectral signatures (absorption coefficients) of component gases in the mixture. This is due primarily because direct overlap of a

discrete laser line with the center of the molecular absorption band is a fortuitous and reasonably rare event. More commonly, a laser line falls on a rapidly decaying edge of the analyte absorption profile. Very small changes from scan to scan in laser parameters can cause slight changes in the lasing frequency and subsequently change the observed absorption coefficient. Hence it becomes highly desirable to provide the ability to weight the coefficients depending on their statistical variance (i.e. on how constant the constant is observed to be, experimentally). However, no strategy for directly weighting the coefficients used in the least squares multivariate analysis has been published. An iterative coefficient weighting strategy has been devised which accomplishes this goal.

Experimental

The iterative procedure begins by setting the weighting matrix W (in Eq. 5) to ones, i.e., no weighting is initially used. The multivariate least squares procedure is used to calculate an initial "guess" of the component concentrations of the mixture. The resultant calculated component concentrations are often in error. A new weighting matrix W is calculated by determining a sum of the variance for each equation. The sum of the variance is calculated by summing the products of each variance coefficient with its calculated concentration value.

$$\sigma_{jT}^2 = \sigma_{Cj1}^2 x_1 + \sigma_{Cj2}^2 x_2 + \dots + \sigma_{Cjn}^2 x_n \quad (\text{Eq. 6})$$

Where σ_{Cji}^2 is the variance of the coefficient of component i at wavelength j and σ_{jT}^2 is the sum of the individual component variances. The reciprocals of the calculated sum variances σ_{jT}^2 are introduced into matrix W and the multivariate least squares procedure is repeated. A new set of component concentrations

is calculated. This iterative procedure is repeated until the component concentrations converge at each successive iteration step.

It will be shown that due to the widely differing variances of coefficients determined for many gases, a coefficient weighting scheme is appropriate. The utility of this method will be examined by comparing it against the simultaneous equations and standard multivariate least squares determinations of actual gas mixtures using the optoacoustic technique to generate the mixture data.

The optoacoustic spectroscopic system used in this study was comprised of a CO₂ laser with a cavity length of 2.7 meters and plasma tube lengths of 2.5 meters. The laser was tuned with a 75 1/mm 1.5 cm² grating (Bausch and Lomb, Rochester, NY). A differential cell comprised of two identical 2.5 cm long x 1.25 cm internal diameter cells connected by a 2.5 cm x .4 cm thick ZnSe circular discs. Microphones used in this study were Knowles BW-1789 miniature microphones (0.6 cm² active area). A PAR 125 light chopper (PAR-EGG, Princeton, NJ) was used to chop the laser beam at a fixed frequency of 260 Hz. Laser power was monitored with a KT-2010 pyroelectric detector (Laser Precision Corp., Yorkville, NY) after passing the beam through a diffuser. The optoacoustic and pyroelectric detector signals were monitored with PAR 126 and 5101 lock-in amplifiers respectively.

Gas mixtures were made by successive dilutions using gas syringes and gas sampling bulbs. Pure gas samples of molecules that are gases at standard temperature and pressure were obtained by flushing gas bulbs with the pure gas. (Pure gases were obtained from Matheson Gas Products, Cucamonga, CA.) Gas samples of molecules that are liquids at standard temperature and pressure were obtained by allowing a small amount of the liquid to equilibrate in a gas-tight sampling bulb. The concentrations of the gas vapor in the bulb were calculated

by using the integrated form of the Clausius-Clapeyron Equation and checking with GC analysis.

Optoacoustic data were taken by scanning the grating with a stepper motor drive with was under computer control. The computer also supervised data collection of the optoacoustic and pyroelectric laser power monitor signal from the lock-in amplifiers. Normalized data (optoacoustic signal divided by the laser power monitor signal) at each laser line was output to performing optoacoustic scans of pure gas samples mixtures. A provision for displaying raw optoacoustic scan data on a Linear 225 strip chart recorder (Linear Instruments, Irvine, CA) was also provided.

Results and Discussion

Absorption coefficients at each laser line were determined by scanning the laser with a pure gas sample in the differential optoacoustic cell. A minimum of four scans was used to determine each coefficient. Average coefficients at selected laser lines used for a four-component mixture analysis are listed in Table I. The standard deviation for each coefficient is also listed. Note that the relative standard deviation for each coefficient of each gas can vary considerably between several different laser lines. Variances of the relative standard deviation for each gas is due to the laser line overlap problem discussed previously. Note that generally the relative standard deviation of coefficients is independent of the magnitude of the coefficient. It can be shown that coefficients with the greatest magnitude will have the most effect in determining the calculated unknown values when using a mathematical technique based on solving sets of linear equations. This supports the contention that an analysis strategy based on a coefficient weighting scheme

might be preferred.

The first system studied consisted of a furan, trichloroethylene, ammonia and freon-12 mixture. Average absorption coefficients at the nine laser lines used in this study are given in Table I. This four component mixture was treated initially using the simultaneous equations numerical procedure. The four optimum laser lines used in this analysis are indicated in Table I. These lines were chosen based on a rejection ratio calculations (3). The rejection ratio is defined as the ratio between the absorption coefficient of a pair of gases at a laser line. An optimum laser line can be chosen for each gas by determining the line which maximizes the rejection ratio for this component with respect to other gas components in the mixture.

The results using the simultaneous equations technique for a four component mixture of freon-12, furan, trichloroethylene and ammonia are shown in Table II. The calculated concentration values for trichloroethylene, furan, and freon-12 agree quite well with the actual concentrations. However the calculated concentration of ammonia was negative. Results of the analysis of this same mixture using the multivariate least squares procedure is also shown in Table II. This analysis procedure used data at the nine lines listed in Table I. Note that a non-negative concentration value for ammonia was determined, however the standard deviation of the calculated concentration of ammonia is quite large (approximately 100% RSD). Thus it could be concluded that ammonia may be present in this mixture but the correct concentration value would be in doubt. This illustrates the utility of the statistical generation aspect of the least squares analysis procedure.

The results of the coefficient weighted iterative least squares procedure on the same four component mixture are shown in Table III. The results of the

first iteration are identical with the unweighted least squares procedure since the weighting matrix W introduced into the analysis initially contained ones in all matrix elements. Successive iteration steps however tended to give concentration values closer to the actual concentrations. By the fourth iteration step all values have converged and are close to the actual concentrations of the gas mixture in the cell. Ammonia was determined with only a 10% concentration error (30% RSD) using this analysis procedure.

The results of another four component mixture of these same three gases using both the simultaneous equations and multivariate analysis is shown in Table IV. In this mixture the concentration of freon-12 was increased by a factor of two and the ammonia concentration was decreased by a factor of two from the previous analysis. The simultaneous equations and multivariate least squares procedure fail to determine ammonia as evidenced by the negative calculated concentration values.

This same four component mixture was determined using the coefficient weighted least squares procedure as shown in Table V. A positive value for the ammonia concentration is evident, although the standard deviation is quite large (70% RSD). The analyst could properly conclude that ammonia was present in this mixture.

To further test the effectiveness of the weighted least squares procedure, a mixture of freon-12, ethylene, ammonia, furan and methanol was added to the optoacoustic cell. The analysis of this mixture could be expected to be difficult considering the magnitude of spectral overlap between these gases, as shown in Fig. 1. The first five component mixture tested consisted of 90 ppm ethylene, 240 ppm ammonia, 70 ppm freon-12, 40 ppm furan and 30 ppm methanol.

Raw coefficients and standard deviations at each of the 20 laser lines used in this analysis are shown in Table VI. Results using all three techniques are shown in Table VII. (The five laser lines used for the simultaneous equations determination are indicated in Table VI.) The results of the simultaneous equations analysis are poor. The concentration of freon-12 was underdetermined by a factor of 10 and the concentration of furan was overdetermined by 100%. The results of the multivariate least squares procedure are better, however methanol was underdetermined by a factor of 3 and freon-12 was overdetermined by 70%.

Results using the iterative coefficient weighted least squares procedure (at the fourth iteration step) on the same mixture are also shown in Table VII. Note that all concentration values are reasonable at the fourth iteration step. The largest error was in the determination of the methanol and freon-12 concentrations, which were in error by 27% and 40% respectively.

A similar five-component mixture in which the concentrations of furan and ammonia were decreased by a factor of 10 and ethylene was increased by a factor of 3 over the previous analysis was analyzed. The results using all three analysis procedures are shown in Table VIII. The results of the simultaneous equations procedure are very poor, for example the concentration of freon-12 was determined to be negative. The results using the multivariate least squares procedure are better. However the concentrations of ammonia was overdetermined by a factor of 5 and the concentration of methanol was underdetermined by a factor of 2. The clear superiority of the iterative coefficient weighted least squares approach is evident by examining Table VIII. All calculated concentration values are reasonably close to the actual values in

the cell by the fourth iteration.

Conclusion

These investigations have demonstrated the poor performance of the simultaneous equations data reduction techniques as compared to the multivariate least squares and the iterative coefficient weighted least squares approach for determining gas mixtures using laser line excited optoacoustic technique. The iterative approach is observed to produce the best results, particularly in the most demanding situations.

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References

1. L. B. Kreuzer, J. Appl. Phys. 42, 2934 (1971).
2. L. B. Kreuzer, N. D. Kenyon and C. K. N. Patel, Science 177, 247 (1972).
3. L. B. Kreuzer, Anal. Chem. 46, 235A (1974).
4. P. Perlmutter, S. Shtrikman and M. Slatkine, Appl. Optics 18, 2267 (1979).
5. L. Sica, Appl. Optics 12, 2848 (1973).
6. P. W. Swyer, Ann. Math. Stat. 15, 82 (1944).
7. J. C. Sternberg, H. S. Skillo and R. H. Schwenden, Anal. Chem. 32, 84 (1960).
8. I. M. Warner E. R. Davidson and G. D. Christian, Anal. Chem. 49, 2155 (1977).
9. D. E. Sands, J. Chem. Ed. 51, 473 (1974).

TABLE I. Coefficients (atm cm)⁻¹ and Standard Deviations^a
at Each Laser Line Used in the Four Component
Mixture Study.

Gas	Laser Line									
	P36-100 ^b	P30-100	P22-100	P14-100 ^b	R24-100	R28-100 ^b	P8-020	R16-020	R26-020 ^b	
Freon	33.2 (6.2)	8.3 (1.0)	0.96 (0.09)	0.83 (0.10)	0.001 (0.001)	0.001 (0.001)	0.26 (0.004)	4.3 (0.52)	14.9 (3.6)	
Trichloroethylene	4.9 (0.53)	5.0 (1.1)	5.6 (1.0)	23.0 (4.1)	8.5 (3.2)	1.6 (0.18)	1.3 (0.21)	0.90 (0.99)	0.30 (0.042)	
Furan	0.08 (0.01)	0.03 (.001)	0.03 (0.001)	0.08 (0.01)	2.6 (0.48)	3.0 (0.98)	1.1 (0.22)	1.3 (0.32)	1.8 (0.21)	
Ammonia	14.5 (2.3)	0.62 (0.15)	0.16 (0.002)	0.63 (0.009)	0.05 (0.004)	0.05 (0.005)	0.20 (0.06)	5.4 (1.1)	46.0 (12.1)	

^a Standard deviations appear in parenthesis under each coefficient.

^b Coefficients at these four laser lines were used in the simultaneous equations analysis.

TABLE II. Comparison of Simultaneous Equations and Multivariate Least Squares for the Analysis Using 9 Laser Lines of the First Four Component Mixture.

Gas Concentrations in Cell (ppm)	Calculated Concentrations (ppm)	
	Simultaneous Equations	Multivariate Least Squares
Freon 12 - 270	394	329 ± 39
Trichloro- ethylene - 66	82	81 ± 6
Furan - 475	403	301 ± 163
Ammonia - 111	-13	47 ± 44

TABLE III. Results at Each Step Using the Iterative Coefficient Weighted Least Squares Analysis for the First Four Component Mixture Using 9 Laser Lines.

Gas Concentrations in Cell:			
X1 = Freon-12		270	ppm
X2 = Trichloroethylene		66	ppm
X3 = Furan		475	ppm
X4 = Ammonia		111	ppm

<u>1st Iteration</u>	<u>3rd Iteration</u>
X1 = 329 ± 39 ppm	X1 = 232 ± 47 ppm
X2 = 81 ± 6 ppm	X2 = 72 ± 8 ppm
X3 = 301 ± 163 ppm	X3 = 379 ± 47 ppm
X4 = 47 ± 44 ppm	X4 = 96 ± 32 ppm

<u>2nd Iteration</u>	<u>4th Iteration</u>
X1 = 236 ± 50 ppm	X1 = 232 ± 46 ppm
X2 = 71 ± 8 ppm	X2 = 72 ± 7 ppm
X3 = 387 ± 39 ppm	X3 = 380 ± 47 ppm
X4 = 88 ± 46 ppm	X4 = 96 ± 32 ppm

TABLE IV. Comparison of Simultaneous Equations and Multivariate Least Squares for the Analysis of the Second Four Component Mixture.

Gas Concentrations in Cell (ppm)		Calculated Concentrations (ppm)	
		Simultaneous Equations	Multivariate Least Squares
Freon-12	430	570	513 \pm 34
Trichloroethy- lene	53	70	68 \pm 5
Furan	750	818	726 \pm 143
Ammonia	56	-64	-12 \pm 38

TABLE V. Results at Each Step Using the Iterative Coefficient Weighted Least Squares Analysis for the Second Four Component Mixture.

Gas Concentrations in Cell:	X1 = Freon-12	430 ppm
	X2 = Trichloroethylene	53 ppm
	X3 = Furan	750 ppm
	X4 = Ammonia	56 ppm

1st Iteration

X1 = 513 ± 34 ppm
X2 = 68 ± 5 ppm
X3 = 726 ± 143 ppm
X4 = -12 ± 38 ppm

3rd Iteration

X1 = 427 ± 54 ppm
X2 = 61 ± 5 ppm
X3 = 784 ± 53 ppm
X4 = 33 ± 22 ppm

2nd Iteration

X1 = 426 ± 56 ppm
X2 = 61 ± 5 ppm
X3 = 787 ± 47 ppm
X4 = 31 ± 49 ppm

4th Iteration

X1 = 427 ± 54 ppm
X2 = 61 ± 5 ppm
X3 = 784 ± 53 ppm
X4 = 33 ± 21 ppm

TABLE VII. Comparison of Simultaneous Equations (SE), Multivariate Least Squares (MLS), and Iterative Coefficient Weighted Least Squares (ICWLS)^a for the Analysis of the First Five Component Mixture Using 20 Laser Lines.

Gas Concentrations in Cell (ppm)		Calculated Concentrations (ppm)		
		SE	MLS	ICWLS
Ethylene	90	119	104 ± 22	97 ± 12
Ammonia	240	239	228 ± 84	235 ± 44
Freon-12	70	7	119 ± 20	72 ± 11
Furan	40	84	30 ± 20	34 ± 8
Methanol	30	34	11 ± 10	29 ± 8

^aResults of the Iterative Coefficient Weighted Least Squares procedure taken at the fourth iteration step.

TABLE VIII. Comparison of Simultaneous Equations (SE), Multivariate Least Squares (MLS), and Iterative Coefficient Weighted Least Squares (ICWLS)^a for the Analysis of the Second Five Component Mixture.

Gas Concentrations in Cell (ppm)		Calculated Concentrations (ppm)		
		SE	MLS	ICWLS
Ethylene	240	416	284 ± 53	248 ± 14
Ammonia	20	70	97 ± 66	22 ± 6
Freon-12	70	-11	96 ± 33	85 ± 22
Furan	4	28	4 ± 3	3 ± 2
Methanol	30	5	15 ± 12	26 ± 5

^aResults of the Iterative Coefficient Weighted Least Squares Procedure taken at the fourth iteration step.

TABLE VI. Raw Absorption Coefficients^a and Standard Deviations^b at Each Laser

Gas	Laser Line (100 Transition)										
	P42 ^c	P40	P38	P36	P14 ^c	P10	R6 ^c	R8	R24	R26	R28
Ethylene	.06 (.01)	.052 (.01)	.055 (.01)	.06 (.005)	.63 (.1)	.63 (.1)	.06 (.002)	.065 (.002)	.21 (.005)	.17 (.005)	.02 (.002)
Ammonia	.66 (.04)	.79 (.064)	.71 (.021)	.67 (.02)	.066 (.9982)	.048 (.0044)	.93 (.052)	.37 (.12)	.006 (.002)	.006 (.002)	.006 (.002)
Freon-12	.37 (.042)	.37 (.037)	.34 (.032)	.27 (.039)	.016 (.0049)	.014 (.0048)	.03 (.01)	.015 (.005)	.012 (.005)	.013 (.003)	.014 (.002)
Furan	.035 (.020)	.049 (.029)	.056 (.029)	.063 (.031)	.105 (.036)	.105 (.031)	.705 (.24)	.60 (.083)	1.34 (.13)	1.10 (.48)	3.76 (.39)
Methanol	.032 (.019)	.027 (.003)	.029 (.0012)	.036 (.0066)	.050 (.005)	.041 (.005)	.10 (.0025)	.19 (.026)	.38 (.022)	.67 (.030)	1.48 (.07)

^a Raw Absorption Coefficients Measured with the Following Pure Gas Concentrations in Opto: Freon-12: 700 ppm; Furan: 400 ppm; Methanol: 600 ppm.

^b Standard Deviations Appear in Parenthesis under each Coefficient

^c These Five Laser Lines were Used in the Simultaneous Equations Analysis of the Five Comp

nts^a and Standard Deviations⁶ at Each Laser Line Used in the Five Component Mixture Study

Line (100 Transition)							Laser Line (020 Transition)							
P10	R6 ^c	R8	R24	R26	R28	P20 ^c	P18	P16	P14	P12	P10	R10	R18	R26 ^c
.63 (.1)	.06 (.002)	.065 (.002)	.21 (.005)	.17 (.005)	.02 (.002)	.04 (.002)	.06 (.003)	.02 (.002)	.01 (.002)	.04 (.002)	.005 (.002)	.005 (.002)	.005 (.002)	.005 (.002)
.048 (.0044)	.93 (.052)	.37 (.12)	.006 (.002)	.006 (.002)	.006 (.002)	.20 (.019)	.15 (.026)	.039 (.017)	.058 (.0043)	.092 (.021)	.099 (.013)	.038 (.004)	.12 (.022)	.046 (.013)
.014 (.0048)	.03 (.01)	.015 (.005)	.012 (.005)	.013 (.003)	.014 (.002)	.02 (.002)	.017 (.003)	.014 (.002)	.017 (.003)	.018 (.003)	.026 (.004)	.10 (.018)	.20 (.055)	.41 (.075)
.105 (.031)	.705 (.24)	.60 (.083)	1.34 (.13)	1.10 (.48)	3.76 (.39)	1.04 (.17)	1.20 (.15)	1.17 (.14)	1.29 (.28)	2.30 (.73)	4.54 (.93)	2.20 (.71)	1.13 (.33)	4.40 (1.73)
.041 (.005)	.10 (.0025)	.19 (.026)	.38 (.022)	.67 (.030)	1.48 (.07)	.86 (.078)	.84 (.11)	.89 (.11)	.96 (.095)	1.95 (.46)	3.57 (.41)	1.07 (.12)	.81 (.14)	.88 (.13)

the Following Pure Gas Concentrations in Optoacoustic Cell: Ethylene: 750 ppm; Ammonia: 1000 ppm; : 600 ppm.

under each Coefficient

multaneous Equations Analysis of the Five Component Mixtures

2